

Maximizing recovery of energy and nutrients from urban wastewaters



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ABSTRACT

Historically, UWWs (urban wastewaters) that contain high levels of organic carbon, N (nitrogen), and P (phosphorous) have been considered an environmental burden and have been treated at the expense of significant energy input. With the advent of new pollution abatement technologies, UWWs are now being regarded as a renewable resource from which, useful chemicals and energy could be harvested. This study proposes an integrated, algal-based system that has the potential to treat UWWs to the desired discharge standards in a sustainable manner while recovering high fraction of its energy content as well as its N- and P-contents for use as fertilizers. Key embodiments of the system being proposed are: i) cultivation of an extremophile microalga, *Galdieria sulphuraria*, in UWW for removal of carbon, N, and P via single-step by mixotrophic metabolism; ii) extraction of energy-rich biocrude and biochar from the cultivated biomass via hydrothermal processing; and, iii) enhancement of biomass productivity via partial recycling of the nutrient-rich AP (aqueous product) from hydrothermal-processed biomass to the cultivation step to optimize productivity, and formulation of fertilizers from the remaining AP. This paper presents a process model to simulate this integrated system, identify the optimal process conditions, and establish ranges for operational parameters.

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1. Introduction

Several recent studies have reported on the feasibility of extending the early efforts of Oswald [1,2] on UWW (urban wastewater treatment) by algal systems towards wastewater treatment coupled with bioenergy generation. The basis of this approach is that, mixed algal/bacterial systems can symbiotically utilize the organic carbon (quantified as BOD (biochemical oxygen demand)), ammoniacal-N, and phosphates in the wastewater and sunlight to synthesize energy-rich biomass which could serve as feedstock for producing gaseous or liquid biofuels via anaerobic digestion [3], catalytic hydrothermal gasification [4], or hydrothermal liquefaction [5]. In contrast to the current fossil fuel-intensive wastewater treatment technologies, this algal-based approach has the potential for sustainable and energy-efficient UWW treatment. Table 1 summarizes the shortcomings of the current technologies and the advantages of the algal system.

1.1. Algal systems for wastewater treatment/energy production

In the 1950s, Oswald, Gotaas [6] had proposed the use of symbiotic algal–bacterial relationship to treat UWW. Their premise was that autotrophic microalgae could serve as photosynthetic aeration units to provide the oxygen for heterotrophic bacteria to oxidize the organic carbon in wastewater releasing CO₂ and nutrients, which in turn, could be utilized by algae to photosynthesize biomass. Oxidation ponds and high rate algal ponds developed on this premise have demonstrated the feasibility of low-cost UWW treatment [7,8]. In the past two decades, many have extended this concept to optimize biomass growth on partially treated UWW as well as on agricultural and industrial wastes for nutrient removal and, more recently, to generate energy from the resulting biomass [9,10].

Algal systems have also been adapted for tertiary treatment of UWW for targeted removal of nutrients [10,11] meeting the discharge standards with minimal energy input. Nutrient removal efficiencies by algal systems have been shown to be comparable to those of other technologies that are more energy-intensive. Wang, Min [12] have evaluated algal systems with raw UWW; primary-

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Table 1

Summary of preliminary experimental results of POWER system vs. typical literature results.

| Feature | Current treatment technologies | Algal/bacterial technology | Comment |
|----------------------------|--|--|---|
| Removing BOD from UWW | Activated sludge (A/S) is the most common technology in use for BOD removal. It requires 1.5 kg O ₂ /kg BOD or 1.48 kW-hr/kg [36] BOD or 0.96 kJ/L | Oxygen for heterotrophic BOD removal is provided by the autotrophic algae. Hence, no energy expended for BOD removal by algal/bacterial (A/B) system. | A/B system conserves fossil fuel-derived energy of 0.96 kJ/L averting GHG release of 0.89 kg CO ₂ /kg BOD. |
| Removing N from UWW | Nitrification/denitrification (N/D) is the most common technology in use for N-removal. It requires 4.6 kg O ₂ /kg N or 13.44 kW-hr/kg N or 1.94 kJ/L [37]. | A/B system does not require external energy for N-removal. | A/B system conserves fossil fuel-derived energy of 1.94 kJ/L averting GHG release of 8.1 kg CO ₂ /kg N. |
| Utilizing C:N ratio in UWW | C:N:P ratio in UWW is 271:27:1 vs. 33:7:1 in A/S. Hence, BOD removal by A/S has to be followed by N/D to meet discharge standards for BOD and N with supplemental carbon supply of 2.47 kg methanol/kg N [37]. | C:N:P ratio of algal biomass 106:16:1 [38] is closer to that of UWW. Hence, A/B system can be readily optimized to meet discharge standards for BOD and N. | A/B system enables single-step treatment of UWW and averts supplemental carbon supply. |
| Harvesting carbon from UWW | A/S dissipates nearly 50% of the valuable organic carbon in UWW to the environment as CO ₂ at the expense of significant energy input of 1.48 kW-hr/kg BOD. | A/B systems can assimilate all of the organic carbon in UWW as well as atmospheric CO ₂ to generate energy-rich biomass. | A/B system can achieve higher carbon to biomass conversion than A/S: 0.30 vs. 0.76 kg/kg BOD. |
| Harvesting energy from UWW | A/S consumes 1.08 kJ/L [3] of energy; anaerobic digestion of waste biomass yields 0.18 kJ/L [39]. Thus, the process is energy-negative. | A/B systems do not consume energy and can capture solar energy via photosynthesis. Thus, the process could be energy-positive. | A/B systems can generate biomass of higher energy density than A/S: 30 MJ/kg vs. 20 MJ/kg [40] |

treated UWW; secondary-treated UWW; and, centrate water from sludge centrifuge, and reported total N-removals of 50.8–82.8%; and P-removals up to 90.6%. Pittman, Dean [8] have reported N-removals of about 90% and P-removals of 80% in primary-treated UWW with *Chlorella vulgaris*. Higher removals by algal systems from nitrogen- and phosphorus-rich wastewaters from a variety of agricultural and industrial sources as well as effluent streams from anaerobic digestion of several waste substrates have been documented [13,14].

Anaerobic digestion of the biomass cultivated in wastewater has been evaluated as a means of recovering its energy content in the form of methane as a gaseous biofuel [15]. More recent studies have reported on the extraction of the lipid content of algal biomass cultivated in wastewaters for use as a feedstock for liquid fuel production followed by anaerobic digestion of the lipid-extracted biomass to produce additional fuel as methane [16–18]. Bohutskyi and Bouwer [19] have estimated that, depending on its lipid content, 55–86% of the energy in algal biomass can be recovered through lipid extraction followed by anaerobic digestion. Energetic advantages of coupling algal wastewater treatment with energy production have been reported upon [20,21]. Sturm and Lamer [21], for example, have concluded that direct energy production from algal biomass cultivated in UWW and the energy savings from avoiding biological nutrient removal can outweigh the energy cost associated with algal cultivation and harvesting. In spite of the potential merits of the algal-based systems, they have not been widely accepted by wastewater utilities due to several limitations.

1.2. Limitations of current algal systems

Currently, the open raceway design is the common choice for low-cost algal cultivation. Driven by paddlewheels to maintain the cultures in suspension, these raceways are often sparged with CEA (CO₂-enriched air) to provide the carbon needs to the cultures. To avoid light drop off in such raceways, the culture depth has to be shallow (<0.4 m) and the cell density has to be low (<0.8 g L⁻¹); both these confines have negative impacts on the overall process. Shallow depths translate to larger footprint and surface areas,

resulting in prohibitive water loss by evaporation. In a study by Posadas, Garcia-Encina [22], carbon and nutrient removals by algal systems were shown to be comparable to conventional treatment technologies, but at a high water footprint (0.5–6.7 L m⁻² d⁻¹). Shallow depths also limit the bubble detention time of the sparged CEA, resulting in poor transfer of CO₂ to the culture and consequently, low biomass productivity and energy yield. In addition, low biomass densities translate to inefficient harvesting in downstream processing, and higher overall costs. Further, open raceways are susceptible to contamination and predation by invaders.

The current pathway for algal biomass-to-biofuel is limited also by the energy extraction processes that involve drying of the harvested wet biomass, cell disruption, and extraction of its lipid content for further processing and refining to yield biofuel. While the energy required for drying wet biomass is prohibitively high, the need to maximize lipid productivity (=biomass productivity×lipid fraction) in the cultivation step has also remained a challenge since cultivation conditions for maximizing biomass productivity are counter to those for maximizing lipid fraction [23].

1.3. Proposed system for algal wastewater treatment/energy production

This study presents a POWER (photosynthetically oxygenated waste-to-energy recovery) system to circumvent most of the above limitations of current algal cultivation systems. The POWER system could be exploited for treating UWW to the required discharge standards and yielding higher net energy than current technologies while recovering valuable nutrients in UWW. Developed specifically for warm and arid environments, the POWER system utilizes GS (*Galdieria sulphuraria*), a heterotrophic and photoautotrophic microalga capable of growing at moderately high temperatures (25–55 °C) [24]. The POWER system incorporates low-cost, closed PBR (photobioreactors) in which the temperatures ranges from 25 to 55 °C due to the passive heat gain [25]. Since GS can tolerate high temperatures, the POWER system averts the cooling requirements of traditional strains cultivated in closed PBRs.

The POWER system utilizes HTL (hydrothermal liquefaction) of wet biomass to recover its energy content as biocrude and biochar, while releasing the nutrients in concentrated dissolved form as a side-stream. The system also includes recycling of a fraction of the nutrients released by HTL to the PBR to optimize the C: N: P ratio in the broth to achieve higher biomass production than previously achieved. The resulting energy-dense biocrude can be mixed with petroleum and refined in traditional refineries into transportation fuels, anaerobically digested, or catalytically gasified for electrical co-generation. A simplified schematic of the POWER system is shown in Fig. 1.

The closed PBR design minimizes evaporative water loss, odor emissions, contamination, invasion, and CO₂ loss. Recycling concentrated nutrients from the HTL process to the PBR enables cultivation of higher biomass densities in UWW in a self-sufficient manner. The photosynthetic capture of sunlight and CO₂ in the PBR augments the capture of the energy content of UWW, potentially yielding higher net energy yield than other emerging options for energy recovery from UWW. Importantly, CO₂ capture in the closed system overcomes the sub-optimal stoichiometric C:N:P ratio in UWW relative to microbial biomass. In contrast to the traditional secondary and tertiary wastewater treatment technologies that suffer from imbalance in C:N:P ratio, the POWER system enables complete N and P removal in a single-stage system by maintaining optimal C:N:P ratio [22,23].

Previous reports by the authors have documented the ability of GS to grow in primary effluent at rates comparable to that in standard artificial growth medium, achieving high nutrient removal efficiencies at removal rates comparable to other strains [25,26]. This paper presents a process model of the POWER system and simulated performance curves.

2. Theoretical background

The model for the POWER system is developed as follows by applying mass and energy balances across its components shown in Fig. 1. The variables are defined in the Appendix.

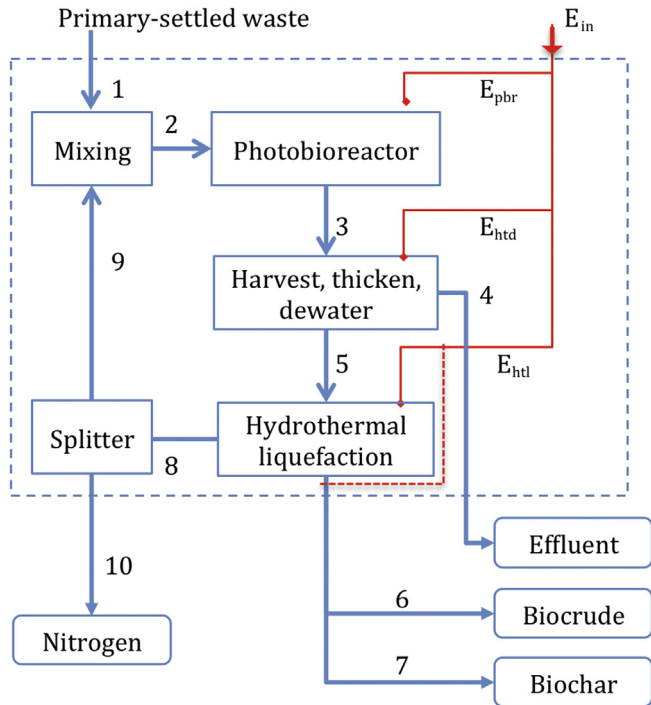


Fig. 1. Schematic of the POWER system for treating primary-settled wastewater and recovering energy and nutrients through hydrothermal liquefaction of the biomass generated. Red lines indicate energy input. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.1. Mass balance on aqueous medium, Q

Mixing:

$$Q_1 + Q_9 = Q_2 \quad (1)$$

Photobioreactor:

$$Q_2 = Q_3 \quad (2)$$

Harvesting, thickening, dewatering:

$$Q_3 = Q_4 + Q_5 \quad (3)$$

Hydrothermal liquefaction:

$$Q_5 = Q_8 \quad (4)$$

Splitter:

$$Q_8 = Q_9 + Q_{10} \quad (5)$$

$$Q_9 = eQ_8 \quad (6)$$

Overall system:

$$Q_1 = Q_4 + Q_{10} \quad (7)$$

2.2. Mass balance on biomass, X

Harvesting, thickening, dewatering:

$$Q_3X_3 = Q_4X_4 + Q_5X_5$$

$$Q_3X_3 = (Q_3 - Q_5)X_4 + Q_5cX_3$$

Which gives

$$Q_5 = \frac{(X_3 - X_4)}{(cX_3 - X_4)} Q_3$$

$$\text{Letting } a = \frac{(X_3 - X_4)}{(cX_3 - X_4)}$$

$$Q_5 = aQ_3 = aQ_2 = a(Q_1 + Q_9) \quad (8)$$

$$Q_4 = (1 - a)Q_3 = (1 - a)Q_2 = (1 - a)(Q_1 + Q_9) \quad (9)$$

2.3. Mass balance on nitrogen, N

Mixing:

$$Q_1N_1 + Q_9N_9 = Q_2N_2 = (Q_1 + Q_9)N_2$$

Which gives

$$N_2 = \frac{Q_1N_1 + Q_9N_9}{(Q_1 + Q_9)} \quad (10)$$

Photobioreactor:

$$Q_2N_2 = Q_3N_3 + Q_3X_3n_3$$

Which gives

$$N_3 = \frac{Q_2N_2 - Q_3X_3n_3}{Q_3} = \frac{Q_3N_2 - Q_3X_3n_3}{Q_3} = N_2 - X_3n_3 \quad (11)$$

Harvesting, thickening, dewatering:

$$Q_3 N_3 + Q_3 X_3 n_3 = [Q_4 N_4 + Q_4 X_4 n_4] + [Q_5 N_5 + Q_5 X_5 n_5] \quad (12)$$

Hydrothermal liquefaction:

$$Q_5 N_5 + Q_5 X_5 n_5 = Bcr_6 n_6 + Bch_7 n_7 + Q_8 N_8 \quad (13)$$

2.4. Yields

Biocrude:

$$Bcr_6 = Y_{Bcr} (Q_5 X_5) \quad (14)$$

Biochar:

$$Bch_7 = Y_{Bch} (Q_5 X_5) \quad (15)$$

Nitrogen:

$$N_{out} = Q_{10} N_{10} = Q_{10} N_8 \quad (16)$$

2.5. Energy

Energy input for photobioreactor:

In this study, the energy input for cultivation in the photobioreactor is considered as that required for mixing and keeping the biomass in suspension. Wide range of energy values (0.09–0.4 kJ L⁻¹) have been reported for cultivation in the literature depending on the type of the cultivation system, culture depth, biomass density, algal strain etc. [9,27,28]. In this study, the energy input for PBRs is assumed as 0.4 kJ L⁻¹ [9].

$$E_{pbr} = 0.4 \quad (17)$$

Energy input for harvesting, thickening, dewatering:

The energy input for harvesting, thickening and dewatering depends on the selected processes and the resulting solids content of the dewatered stream. Microalgae can be harvested using several methods such as flotation, sedimentation, flocculation with organic/inorganic flocculants, centrifugation, and filtration. Typical energy requirements reported in the literature for common harvesting processes are summarized in Table 2. Based on the energy values reported by Quinn, Smith [29] (using passive settling, dissolved air flotation and centrifugation), the energy input for harvesting, thickening and dewatering, E_{htd} , in this study was assumed as follows: 2.4 kJ L⁻¹, 4.8 kJ L⁻¹, 10.7 kJ L⁻¹, or 16.6 kJ L⁻¹ to achieve solids contents of 5%, 10%, 15%, and 20%, respectively.

Energy input for hydrothermal liquefaction:

The energy input to the HTL process is assumed to be that for raising the temperature of the feed from ambient temperatures to the selected HTL processing temperature, T_{htl} . It is also assumed that losses are negligible, and heat energy is recovered from the HTL effluent to preheat the feed at a heat recovery of η . The specific heat and the density of the medium are assumed to be those of water. Thus,

$$E_{htl} = (1 - \eta) \{ Q_5 C_{p,w} \rho_w (T_{htl} - T_{amb}) \} \quad (18)$$

Thus, total energy input:

$$E_{in} = E_{pbr} + E_{htd} + E_{htl} \quad (19)$$

Energy output in the form of biocrude:

$$E_{Bcr} = HHV_{Bcr} Bcr_6 \quad (20)$$

Energy output in the form of biochar:

$$E_{Bch} = HHV_{Bch} Bch_7 \quad (21)$$

Thus, total energy output:

$$E_{out} = E_{Bcr} + E_{Bch} \quad (22)$$

Net energy:

$$E_{net} = E_{out} - E_{in} \quad (23)$$

Energy ratio:

$$ER = \frac{E_{out}}{E_{in}} \quad (24)$$

From the above equations, the following expression for ER can be derived:

$$ER = \frac{a c \{ Y_{Bcr} HHV_{Bcr} + Y_{Bch} HHV_{Bch} \}}{(1 - a e) \{ E_{pbr} + E_{htd} \} + (1 - \eta) a C_{p,w} \rho_w (T_{htl} - T_{amb})} X_3 \quad (25)$$

where, yields of biocrude (Y_{Bcr}) and biochar (Y_{Bch}) are functions of the HTL process temperature, T_{htl} . Currently, the temperature-dependence of the yields have to be established empirically; the following correlations established from our experimental studies with GS over a HTL process temperature range of 180 °C–300 °C are used in this study [30]:

Biocrude [g/g]:

$$Y_{Bcr} = 3.35 - 3 \times 10^{-7} T_{htl}^3 + 2 \times 10^{-4} T_{htl}^2 - 4.6 \times 10^{-2} T_{htl}; \quad r^2 = 0.998 \quad (26)$$

Biochar [g/g]:

$$Y_{Bch} = 9.654 \exp(-0.014 T_{htl}); \quad r^2 = 0.966 \quad (27)$$

The 3rd order polynomial relationship between biocrude yield and temperature ($p < 0.005$) is typical of common algal strains (as can be derived from the data reported by Alba, Torri [31] and Christensen, Peng [32]) tracking an increase in yield with temperature up to a point and decline thereafter due, in part, to loss of carbon via the gas phase. Christensen, Peng [32] have, for example, reported that gas yield increased with T_{htl} , and its methane content increased from 3% at 400 °C to 7% at 420 °C. The above correlations derived using calibration data (from Ref. [30]) were validated with an independent validation dataset collected in this study. Results of this validation test are summarized in Fig. 2 showing that the above correlations are able to predict satisfactorily the temperature-dependence of biocrude yield (Fig. 2a, $r^2 = 0.992$) and biochar (Fig. 2b; $r^2 = 0.921$).

For a given harvesting, thickening, dewatering system that can achieve a desired concentrating factor c , the key operational parameters of the POWER system can be seen as the biomass density at harvest, X_3 ; the HTL process temperature, T_{htl} ; the aqueous split

Table 2
Energy input as a function of outlet solids content for common harvesting processes.

| Harvesting process | Outlet solids content [%] | Energy input [kJ/L] | Ref. |
|--------------------------|---------------------------|---------------------|---------|
| Flotation | 10 | 4.8 | [29] |
| Coagulation/flocculation | 4 to 10 | 0.19 to 3.24 | [41–43] |
| Filtration | 8 to 27 | 0.36 to 3.17 | [3] |
| Centrifugation | 0.4 to 22 | 1.08–22 | [44] |

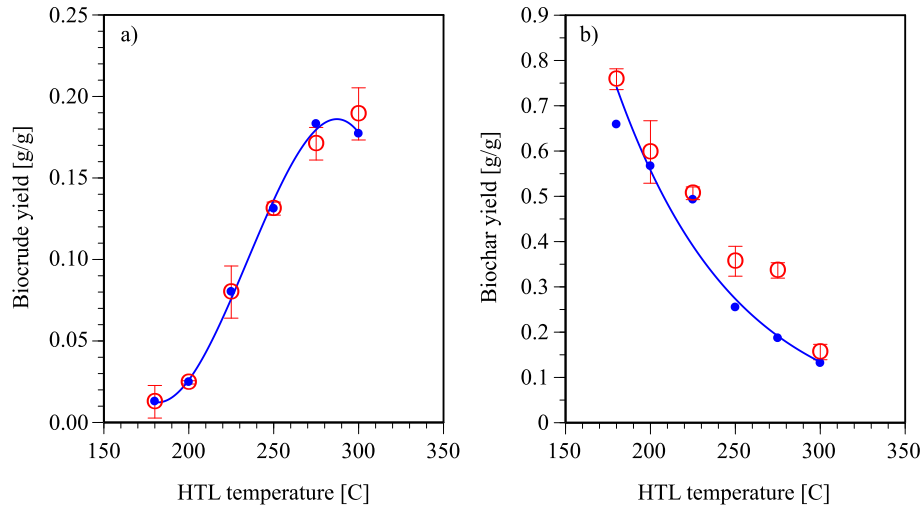


Fig. 2. Validation of correlation models: a) for biocrude yield, Equation (26); and b) for biochar, Equation (27). • indicates datasets used for calibration; ○ indicates datasets used for validation; curves represent correlations derived from calibration data set; error bars determined from triplicates for validation dataset.

fraction, e ; and the heat recovery from the HTL effluent, η . Since the expression for ER (Equation (25)) is not intuitive to gain insights into the integrated process or to discern the sensitivity of the key operational parameters, simulations were done and the results were evaluated graphically.

3. Results and discussion

The mass and energy balance equations developed above were simulated with the following simplifying assumptions. Biomass density in the clarified effluent of the harvesting, thickening, dewatering step, X_4 is assumed to be 0.001 g L^{-1} ; N_4 is assumed to be 0.005 g L^{-1} ; higher heating value of biocrude is assumed as 30 MJ kg^{-1} and that of biochar, as 18 MJ kg^{-1} ; energy required for cultivation, E_{pbr} , is assumed a constant of 0.4 kJ L^{-1} ; specific heat of the broth is assumed as that of water = $4.19 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$; density of the broth is assumed as that of water = 1000 kg m^{-3} ; heat recovery from the HTL product stream is assumed as 60%; the fraction of the aqueous product of HTL that is recycled is assumed as 0.5; biomass content in the UWW was assumed negligible; complete conversion of biomass by HTL was assumed (i.e. $X_6 = 0$; $X_7 = 0$; $X_8 = 0$; $X_9 = 0$; and $X_{10} = 0$);

3.1. ER as a function of process variables

Fig. 3 illustrates the dependence of the energy ratio on HTL process temperature, biomass density at harvest, and the solids content after harvesting, thickening and dewatering. For any biomass density and solids content, the lowest temperature of $180 \text{ }^\circ\text{C}$ is seen as optimal on the basis of total energy input and total energy output from biocrude and biochar (bold columns in Fig. 3). This result is primarily due to the fact that the increase in energy yield realized at higher temperatures is not justified by the additional thermal energy expended for heating; even with lower thermal energy input at higher solid contents with lower volumes of water, the return on energy yields is not high enough.

As predicted by Equation (25), the energy ratio can be seen to increase with biomass density at harvest, X_3 . Increase in biomass density increases total energy output per unit volume of liquid handled. However, irrespective of biomass density, for any given HTL temperature, the energy ratio is seen to be optimal at a solids content of 10%. At low solid contents with high water volumes, more thermal energy has to be expended for heating the feed to HTL; on the other hand, at higher solid contents, more energy has to be expended in harvesting/dewatering/thickening. Another reason is that the biocrude yield

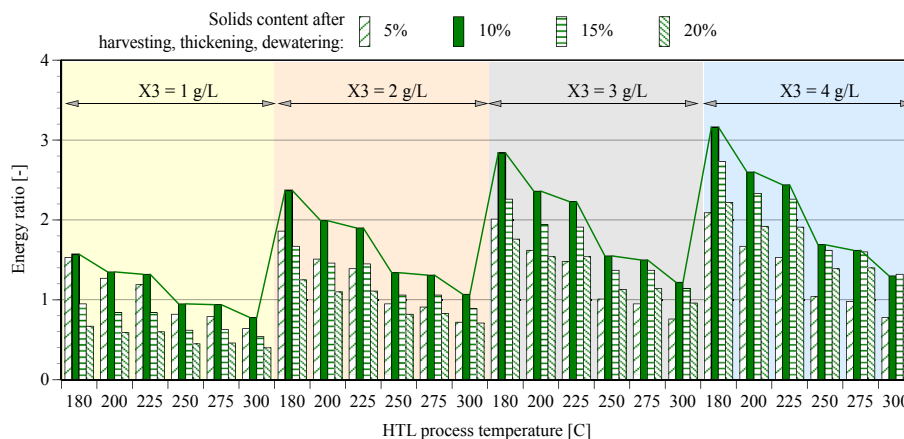


Fig. 3. Energy ratio, ER, as a function of HTL process temperature, T_{hlt} ; biomass density at harvest, X_3 ; and solids content after harvesting/thickening/dewatering.

increases with temperature first and falls off with further increase of temperature (Equation (26)) due to loss of carbon via gas phase. This finding agrees with most literature reports that had evaluated HTL at a solids content of 10%. Based on the above analysis, the optimal conditions for maximizing ER under the assumed conditions can be seen to be biomass density at harvest of 4 g L^{-1} , the solids content fed to the HTL process of 10%, and the HTL process temperature of 180°C . This analysis does not take into account the variation of the composition of the biocrude with HTL temperature.

3.2. Effect of HTL temperature

Even though the above analysis suggests that hydrothermal processing of the biomass at low temperatures results in higher energy ratio based on net energy considerations, most of the energy output at low temperatures is associated with biochar than with biocrude. Fig. 4 illustrates the breakdown of the energy components at 180°C as a function of biomass density at harvest, X_3 , at a solids content of 10%, for example. In this example, nearly 97% of the energy output is associated with biochar at X_3 of 4 g L^{-1} . Since biocrude is preferable over biochar as an energy carrier, options to

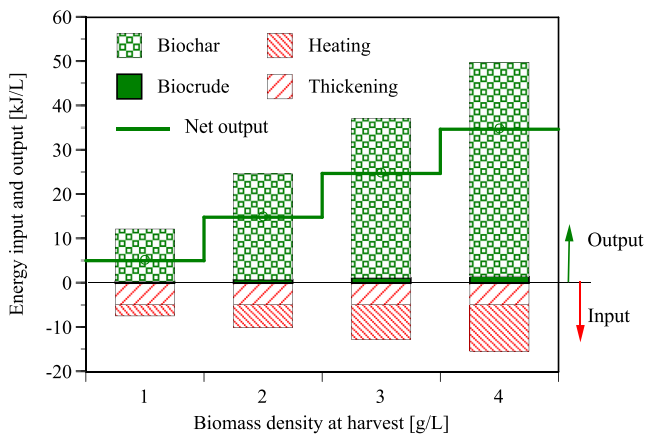


Fig. 4. Energy input and output as a function of biomass density at harvest. HTL process temperature = 180°C ; solids content after harvesting/thickening/dewatering = 10%.

minimize biochar and maximize biocrude need to be deployed to make the POWER system viable as a net energy-producer.

Recent studies have shown that a two-step HTL process wherein, isolation of the polysaccharides released during low-temperature hydrothermal processing followed by high-temperature hydrothermal processing of the remainder can yield higher net yields of biocrude and hence, higher energy ratios. The rationale behind the two-step HTL process is that polysaccharides are believed to contribute to biochar formation and lower net energy balance [5]. Further, polysaccharides can serve better as a valuable source of co-products rather than an energy source.

As part of this study, experiments were conducted to evaluate the feasibility of adopting the two-stage HTL process in the POWER system; the first stage was conducted at 180°C and the second, at 300°C . Biocrude and biochar yields determined in these experiments were used in the model simulations to estimate the net energy yields. Results of these simulations are summarized in Fig. 5 illustrating the improvement in biocrude yields via two-stage HTL processing. These results also suggest that solids content of 10% to be optimal at any biomass density; and that the net energy yield increased with biomass density. Based on these simulations, it is plausible that energy-positive UWW could be achieved if the biomass density is maintained above 2 g L^{-1} .

3.3. Maximizing biomass density

When biomass is cultivated in UWW, a fundamental consideration to maximize biomass density is matching the C:N:P ratio of the biomass to that in UWW. While the C:N:P ratio in algal biomass is closer to that of UWW than in traditional activated sludge biomass, recycling of carbon and nutrients solubilized in the HTL process to the cultivation step as envisioned in the POWER system provides for optimal balancing of C:N:P ratio to maximize biomass productivity and hence the energy yield [33–35]. The POWER system thus enables removal of organic C, N, and P from UWW in a single-step whereas, the traditional wastewater treatment approach involves two steps—activated sludge for organic carbon removal followed by nitrification/denitrification for N removal with supplemental carbon input to balance the C:N:P ratio between UWW and biomass.

The embodiments in the POWER system hold promise for maintaining biomass densities of 2 g L^{-1} through mixotrophic metabolism, nutrient recycling, and carbon management. We have

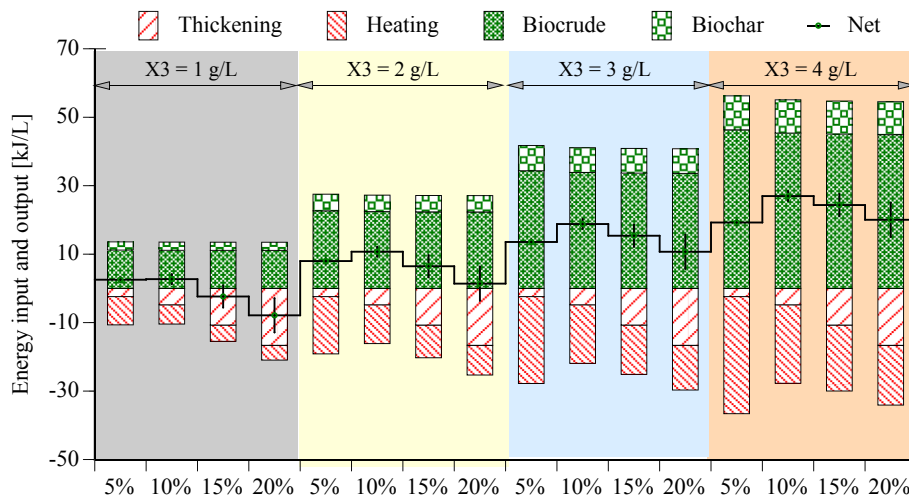


Fig. 5. Energy input and output as a function of solids content and biomass density under two-stage hydrothermal processing: first stage at 180°C and second stage at 300°C . Vertical bars indicate the sensitivity of net energy to $\pm 30\%$ uncertainty in Ehtd.

demonstrated that GS biomass density under mixotrophic conditions exceeded 2 g L^{-1} and the corresponding aerial productivity exceeded $56 \text{ g m}^{-2} \text{ d}^{-1}$ in our outdoor PBRs [34].

3.4. Optimizing energy ratio

Equation (25) indicates that maximizing the biomass density at harvest, X_3 , and the concentrating factor, c , as two options to maximize the energy ratio. While the maximum biomass density in the traditional raceway systems is limited by the need to ensure adequate sunlight penetration for autotrophic growth, mixotrophic metabolism envisioned in the POWER system enables higher densities to be achieved as demonstrated above.

The concentrating factor is an important parameter in energy considerations as high concentrating factors can reduce the volume of water that must be heated for hydrothermal processing; but on the other hand, they demand higher energy input in the harvesting, thickening, and dewatering step. In this study, energy input for harvesting, thickening, and dewatering, E_{htd} , was considered to be dependent only on the resulting solids content. A sensitivity analysis was performed in this study to assess the variation in net energy due to $\pm 30\%$ uncertainty in the assumed E_{htd} . Results of this sensitivity analysis are represented by the vertical bars in Fig. 5 indicating that the uncertainty energy ratio averaged 14% over the temperature range considered here. The impact of E_{htd} on net energy is seen to be negligible at 5%–10% solids content, but increased as solids content increased. Nevertheless, availability of energy-efficient and sustainable harvesting, thickening, and dewatering technology can improve the overall energetics of the integrated process.

4. Conclusions

The results of this study indicate that the POWER system holds promise for improved energy recovery from UWW to make the wastewater treatment process energy-positive and sustainable. The simulation approach presented here established ranges of process parameters for optimal operation of the system and identified harvesting and HTL processing of the biomass as critical components of the POWER system. The following conditions were found to yield maximum energy ratio: biomass harvesting density of 4 g L^{-1} ; solids content of 10% in the feed to the HTL process; and, HTL process temperature of 180°C . For energy-positive wastewater treatment, the biomass harvest density should be at least 2 g L^{-1} and the solids content in the feed to the HTL process should be at least 10%. The ability to recycle carbon and nutrients in the POWER process configuration enables biomass densities to be maintained above 2 g L^{-1} . Two-stage HTL processing (first stage at 180°C and 2nd stage at 300°C) is recommended for increasing yield of biocrude.

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Appendix I. Parameters used in model development

| | |
|------------------|--|
| B_{Bch} | Mass flow rate of biochar [g d^{-1}] |
| B_{Bcr} | Mass flow rate of biocrude [g d^{-1}] |

| | |
|---------------------------|---|
| c | Concentrating factor = $X_5/X_3 = 12.5$ to 200 [–] |
| $C_{p,w}$ | pecific heat of water [$\text{kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$] |
| e | Recycle factor = Q_9/Q_8 |
| E | Energy flow [kJ L^{-1}] |
| HHV_{Bch} | High heating value of biochar [MJ kg^{-1}] |
| HHV_{Bcr} | High heating value of biocrude [MJ kg^{-1}] |
| n | Nitrogen content of biomass [g g^{-1}] |
| n_{Bch} | Nitrogen content of biochar [g g^{-1}] |
| n_{Bcr} | Nitrogen content of biocrude [g g^{-1}] |
| N | Dissolved nitrogen concentration [g L^{-1}] |
| Q | Flow rate of medium [L d^{-1}] |
| T_{amb} | Ambient temperature [$^\circ\text{C}$] |
| T_{htl} | HTL process temperature [$^\circ\text{C}$] |
| X | Biomass concentration [AFDW g L^{-1}] |
| Y_{Bcr} | Yield of biocrude [g g^{-1}] |
| Y_{Bch} | Yield of biochar [g g^{-1}] |

II Nomenclature

| | |
|-------|--|
| AFDW | Ash-free dry weight |
| AP | Aqueous phase |
| CEA | CO_2 -enriched air |
| GS | Galdieria sulphuraria |
| HTL | Hydrothermal liquefaction |
| PBR | Photobioreactor |
| POWER | Photosynthetically oxygenated waste to energy recovery |
| UWW | Urban wastewater |

References

- [1] Oswald WJ. Microalgae and waste-water treatment. In: Borowitzka MBL, editor. Micro-algal biotechnology. Cambridge: Cambridge University Press; 1988. p. 305–28.
- [2] Oswald WJ, Gotaas HB, Ludwig HF, Lynch V. Algae symbiosis in oxidation ponds: photosynthetic oxygenation. Sew Industrial Wastes 1953;25(6): 692–705.
- [3] McCarty PL, Bae J, Kim J. Domestic wastewater treatment as a net energy producer-can this be achieved? Environ Sci Technol 2011;45(17):7100–6.
- [4] Elliott DC. Catalytic hydrothermal gasification of biomass. Biofuels Bioprod Biorefining 2008;2(3):254–65.
- [5] Biller P, Ross AB. Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. Bioresour Technol 2011;102(1):215–25.
- [6] Oswald WJ, Gotaas HB, Golueke CG, Kellen WR, Gloyne EF, Hermann ER. Algae in waste treatment [with discussion]. Sew Industrial Wastes 1957;29(4): 437–57.
- [7] Hoffmann JP. Wastewater treatment with suspended and nonsuspended algae. J Phycol 1998;34(5):757–63.
- [8] Pittman JK, Dean AP, Osundeko O. The potential of sustainable algal biofuel production using wastewater resources. Bioresour Technol 2011;102(1): 17–25.
- [9] Beal CM, Stillwell AS, King CW, Cohen SM, Berberoglu H, Bhattarai RP, et al. Energy return on investment for algal biofuel production coupled with wastewater treatment. Water Environ Res 2012;84(9):692–710.
- [10] Clarens AF, Resurreccion EP, White MA, Colosi LM. Environmental life cycle comparison of algae to other bioenergy feedstocks. Environ Sci Technol 2010;44(5):1813–9.
- [11] Kim J, Lingaraju BP, Rheume R, Lee J-Y, Siddiqui KF. Removal of ammonia from wastewater effluent by Chlorella vulgaris. Tsinghua Sci Technol 2010;15(4):391–6.
- [12] Wang LA, Min M, Li YC, Chen P, Chen YF, Liu YH, et al. Cultivation of green algae Chlorella sp in different wastewaters from municipal wastewater treatment plant. Appl Biochem Biotechnol 2010;162(4):1174–86.
- [13] Cai T, Park SY, Li Y. Nutrient recovery from wastewater streams by microalgae: status and prospects. Renew Sustain Energy Rev 2013;19:360–9.
- [14] Markou G, Georgakakis D. Cultivation of filamentous cyanobacteria (blue-green algae) in agro-industrial wastes and wastewaters: a review. Appl Energy 2011;88(10):3389–401.
- [15] Golueke CG, Oswald WJ, Gotaas HB. Anaerobic digestion of algae. Appl Microbiol 1957;5(1):47.
- [16] Dalrymple OK, Halfhide T, Udom I, Gilles B, Wolan J, Zhang Q, et al. Wastewater use in algae production for generation of renewable resources: a review and preliminary results. Aquat Biosyst 2013;9(1):2.
- [17] Bhatt NC, Panwar A, Bisht TS, Tamta S. Coupling of algal biofuel production with wastewater. Sci World J 2014;2014:210504.

- [18] Zhao B, Ma J, Zhao Q, Laurens L, Jarvis E, Chen S, et al. Efficient anaerobic digestion of whole microalgae and lipid-extracted microalgae residues for methane energy production. *Bioresour Technol* 2014;161:423–30.
- [19] Bohutskiy P, Bouwer E. Biogas production from algae and cyanobacteria through anaerobic digestion: a review, analysis, and Research needs. *Advanced biofuels and Bioproducts*: Springer. 2013. p. 873–975.
- [20] Menger-Krug E, Niederste-Hollenberg J, Hillenbrand T, Hiessl H. Integration of microalgae systems at municipal wastewater treatment plants: implications for energy and emission balances. *Environ Sci Technol* 2012;46(21):11505–14.
- [21] Sturm BSM, Lamer SL. An energy evaluation of coupling nutrient removal from wastewater with algal biomass production. *Appl Energy* 2011;88(10):3499–506.
- [22] Posadas E, Garcia-Encina PA, Soltan A, Dominguez A, Diaz I, Munoz R. Carbon and nutrient removal from centrates and domestic wastewater using algal-bacterial biofilm bioreactors. *Bioresour Technol* 2013;139:50–8.
- [23] Hu Q, Sommerfeld M, Jarvis E, Ghirardi M, Posewitz M, Seibert M, et al. Microalgal triacylglycerols as feedstocks for biofuel production: perspectives and advances. *Plant J* 2008;54(4):621–39.
- [24] Toplin JA, Norris TB, Lehr CR, McDermott TR, Castenholz RW. Biogeographic and phylogenetic diversity of thermoacidophilic Cyanidiales in Yellowstone National Park, Japan, and New Zealand. *Appl Environ Microbiol* 2008;74(9):2822–33.
- [25] Selvaratnam T, Pegallapati A, Montelya F, Rodriguez G, Nirmalakhandan N, Lammers PJ, et al. Feasibility of algal systems for sustainable wastewater treatment. *Renew Energ* 2015;82(0):71–6.
- [26] Selvaratnam T, Pegallapati AK, Montelya F, Rodriguez G, Nirmalakhandan N, Van Voorhies W, et al. Evaluation of a thermo-tolerant acidophilic alga, *Galdieria sulphuraria*, for nutrient removal from urban wastewaters. *Bioresour Technol* 2014;156(0):395–9.
- [27] Frank ED, Han J, Palou-Rivera I, Elgowainy A, Wang MQ. Life-Cycle analysis of algal lipid fuels with the greet model. *Energy Systems Division - Argonne National Laboratory*; 2011. p. 1–99.
- [28] Lundquist TJ, Woertz IC, Quinn NWT, Benemann JR. A Realistic technology and engineering assessment of algae biofuel production. *Energy Biosciences Institute*; 2010. p. 1–178.
- [29] Quinn JC, Smith TG, Downes CM, Quinn C. Microalgae to biofuels lifecycle assessment — Multiple pathway evaluation. *Algal Res* 2014;4(0):116–22.
- [30] Reddy HK. Production of liquid transportation fuels from wet algae. New Mexico State University: New Mexico State University; 2013.
- [31] Alba LG, Torri C, Samori C, van der Spek J, Fabbri D, Kersten SRA, et al. Hydrothermal treatment (HIT) of microalgae: evaluation of the process as conversion method in an algae biorefinery concept. *Energy Fuels* 2012;26(1):642–57.
- [32] Christensen PS, Peng G, Vogel F, Iversen BB. Hydrothermal liquefaction of the microalgae *Phaeodactylum tricornutum*: impact of reaction conditions on product and elemental distribution. *Energy Fuels* 2014;28(9):5792–803.
- [33] Selvaratnam T, Pegallapati AK, Reddy H, Kanapathipillai N, Nirmalakhandan N, Deng S, et al. Algal biofuels from urban wastewaters: maximizing biomass yield using nutrients recycled from hydrothermal processing of biomass. *Bioresour Technol* 2015;182(0):232–8.
- [34] Henkanatte-Gedera SM, Selvaratnam T, Caskan N, Nirmalakhandan N, Van Voorhies W, Lammers PJ. Algal-based, single-step treatment of urban wastewaters. *Bioresour Technol* 2015;189(0):273–8.
- [35] Selvaratnam T, Reddy H, Muppaneni T, Holguin FO, Nirmalakhandan N, Lammers PJ, et al. Optimizing energy yields from nutrient recycling using sequential hydrothermal liquefaction with *Galdieria sulphuraria*. *Algal Res* 2015;12:74–9.
- [36] Tchobanoglous G, Burton FL, Stensel HD. *Wastewater Engineering: treatment and reuse*, Metcalf & Eddy. 4 ed. Boston: McGraw-Hill; 2003.
- [37] Kang SJ, Olmstead K, Takacs K, Collins J. Municipal nutrient removal technologies reference document. 2008 (EPA 832-R-08–006).
- [38] Tett P, Droop MR, Heaney SI. The redfield ratio and Phytoplankton growth rate. *J Mar Biol Assoc U. K* 1985;65(02):487–504.
- [39] Remy C, Boulestreau M, Lesjean B. Proof of concept for a new energy-positive wastewater treatment scheme. *Water Sci Technol* 2014;70(10):1709–16.
- [40] Mahmood T, Elliott A. A review of secondary sludge reduction technologies for the pulp and paper industry. *Water Res* 2006;40(11):2093–112.
- [41] Shuman TR, Mason G, Marsolek MD, Lin Y, Reeve D, Schacht A. An ultra-low energy method for rapidly pre-concentrating microalgae. *Bioresour Technol* 2014;158(0):217–24.
- [42] Poelman E, De Pauw N, Jeurissen B. Potential of electrolytic flocculation for recovery of micro-algae. *Resour Conserv Recycl* 1997;19(1):1–10.
- [43] Vandamme D, Pontes SCV, Goiris K, Foubert I, Pinoy LJJ, Muylaert K. Evaluation of electro-coagulation-flocculation for harvesting marine and freshwater microalgae. *Biotechnol Bioeng* 2011;108(10):2320–9.
- [44] Borowitzka MA, Moheimani NR. *Algae for biofuels and energy*. Springer. Netherlands: Springer; 2013.